

# **An Endstation for Controlled Environment**

## **X-ray Absorption Spectroscopy at 2-5 keV on BL 9.3.1**

Karen L. McFarlane, Melvin P. Klein, and Vittal K. Yachandra  
Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

### **BACKGROUND**

X-ray absorption spectroscopy (XAS) is an element-specific technique with widespread applications in structural biology. Most notably, it has been used in the hard X-ray region ( $>6$  keV) to probe metal centers in metalloproteins. In contrast, investigations of low-Z atoms (e. g., S, Cl, Ca) within proteins and other biological samples have been scarce. Such experiments require the use of a cryostat with vacuum insulation since low temperatures are required for protein samples to minimize radiation damage and for data collection in the EXAFS region. Existing instrumentation does not allow substantial transmittance of intermediate X-rays through the windows to reach the sample, which inhibits adequate flux of fluorescent X-rays to reach the detector.

### **DESCRIPTION**

A new end station on Beamline 9.3.1 at the ALS has been designed and built for such XAS experiments in the 2-5 keV region for solid, liquid or solution samples under selectable temperature and pressure. The sample chamber is mounted to a liquid helium cryostat enabling spectra collection at any temperature between 10 K and room temperature. A gas manifold connected to the sample chamber allows the experimenter to choose a gas at any pressure up to 1 atm or vacuum. Sample changes can be performed in minutes.

To minimize attenuation of the incoming X-rays the sample chamber has a single thin window between the beam line vacuum and the sample. Most X-ray absorption spectra are observed by fluorescence detection of X-rays characteristic of the element under study, and thus we have incorporated a Si photodiode detector inside the sample chamber to avoid another exit window. The internal detector is situated 1 cm away from the sample, which allows collection of a large solid angle of fluorescent X-rays. There are also provisions for a thin exit window for use with an externally mounted detector. In this configuration, the advantage of energy resolution offsets the disadvantage of lower signal output due to absorption by the extra window. A

retractable Si photodiode downstream from the internal sample chamber may be used for transmission experiments or sample positioning.

Because small shifts in the precise energy of features in the X-ray absorption near edge structure (XANES) often reveal significant chemical information, precise energy referencing from scan-to-scan and from run-to-run is required. Immediately upstream from the sample chamber, a smaller chamber houses standard compounds whose spectral features serve to calibrate beam energy. This technique suffices for low resolution studies, but for more exacting studies we have incorporated a Si crystal mounted on the slits at fixed angle relative to both the incident beam and to a detector. As the beam line monochromator scans energy, the diffraction “glitches” which occur provide very sharp energy markers.

Incident beam intensity is measured either by photo-emission from a metal mesh or by creating a small ionization chamber between two polymer windows that can be inserted into the incident beam path. The gas ionization chamber can also be used as a sample space for collecting spectra of gaseous samples.

## **TESTING AND FUTURE WORK**

The new instrumentation has been used to collect spectra for solid materials at the S, Cl, and Ca K-edges, for Ar gas at the Ar K-edge, and the three L-edges of Xe. The cryostat has been tested at temperatures down to 10 K for use with frozen solutions. Future experiments will include frozen solutions of metalloproteins and inorganic model complexes in which we will measure spectra at the S, Cl, and Ca K-edges and Mo L-edges.

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Vittal K. Yachandra and Melvin P. Klein, Physical Biosciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720. [VKYachandra@LBL.gov](mailto:VKYachandra@LBL.gov) or [MPKlein@LBL.gov](mailto:MPKlein@LBL.gov). Tel: (510) 486-4330 Fax: (510) 486-6059